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On the influence of hydrogen on the erbium-related luminescence in silicon

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Erbium- and oxygen-doped silicon was additionally doped with hydrogen, using plasma-enhanced chemical vapor deposition. Samples treated with solid-phase epitaxy (SPE) before hydrogenation and annealing at 900 °C afterwards show a large enhancement of the photoluminescence (PL) yield. A change in local concentration leads to a dominance of the cubic center in the PL. Controlled etching shows that the PL stems from a deeper region with lower erbium concentration. The luminescence yield in the hydrogenated samples is significantly higher, even compared to samples optimized for cubic center luminescence. We thus conclude that hydrogen enhances the solubility of the cubic center in Si:Er,O. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1596380]

Erbium-doped semiconductors have attracted a lot of attention as they allow one to obtain temperature-stable emission at a well-defined wavelength.[1–7] Furthermore, the wavelength close to 1.5 μm of this emission, stemming from an intra-4f transition, coincides well with the absorption minimum in conventional optical fibers. The main problem for applying this material system to devices working at room temperature is the temperature-induced quenching of the luminescence efficiency. Investigations showed that codoping of Si with Er and light elements, in particular oxygen, leads to a reduction of this quenching;[3] RT electroluminescence (EL) and photoluminescence (PL)[4,5] were subsequently reported. The low solubility limit of Er in Si necessitates the use of nonequilibrium methods, such as ion implantation, for its incorporation. After implantation, because of the required high doses for Er and O, a thermal annealing step for recrystallization is necessary. To achieve RT EL, Er has to be incorporated in $SiO_{2-\delta}$ precipitates, which are formed at high annealing temperatures (>950 °C).[6] Both Er and O stay relatively immobile even at temperatures that high. The shallow dopants required for a diode structure, however, already show substantial diffusion at this temperature.[7] Hydrogen is a very common impurity in all semiconductor materials. Among its positive characteristics, there are gettering of metal impurities and passivation of residual defects,[8] as well as the known enhancement of the diffusion of interstitial oxygen.[9] Therefore, we expected a positive effect on the formation of Er–O complexes and precipitates, and thus generally on the performance of EL devices. We also hoped that hydrogen might decrease the necessary annealing temperature for precipitate formation, thus helping to prevent diffusion of the dopants.

Starting material was boron-doped 10-Ω cm (100) Czochralski-Si. The wafers were implanted with Er at 300 keV and a dose of 3×10^{14} cm^{-2}, and oxygen at 40 keV to a dose ten times that of erbium. The peak concentrations estimated by TRIM code simulations were 1.5×10^{18} and 1.5×10^{19} cm^{-3}, respectively. The implantation energies were chosen to achieve spatial overlap for the doping profiles and led to peak concentrations residing at a depth of 150 nm. After the initial implantation one set of samples (set 1) was annealed at 600 °C for 15 min in nitrogen atmosphere for recrystallization using solid-phase epitaxy (SPE); a second set (set 2) remained untreated. Both sets were then hydrogenated for 1 h at 260 °C using plasma-enhanced chemical vapor deposition, leading to a hydrogen content of about 10^{19} cm^{-3} throughout the samples.[10] After hydrogenation, the samples were again annealed at temperatures ranging from 400 to 1000 °C. Results for the hydrogenated samples were compared to those of similarly prepared reference samples without hydrogenation. A list for the differently prepared sets of samples is given in Table I. PL measurements were carried out using the 514.5-nm line of an Ar^+-ion laser at temperatures between 10 and 200 K. The spectra were taken using a BOMEM DA8 Fourier spectrometer and an LN_2-cooled Ge detector.

TABLE I. Description of sample preparation.

Set	Implant. doses of Er (300 keV) and O (40 keV) [cm^{-2}]	SPE	Hydrogen Treatment	Anneal Temp. [°C]
1	3×10^{14} cm^{-2} 3×10^{15} cm^{-2}	Yes	260 °C/ 1 h	$\leqslant$1000
2	3×10^{14} cm^{-2} 3×10^{15} cm^{-2}	No	260 °C/ 1 h	$\leqslant$1000
3	3×10^{14} cm^{-2} 3×10^{15} cm^{-2}	Yes	No	$\leqslant$1000
4	3×10^{14} cm^{-2} 3×10^{15} cm^{-2}	No	No	$\leqslant$1000
5	1×10^{13} cm^{-2} 1×10^{14} cm^{-2}	No	No	900

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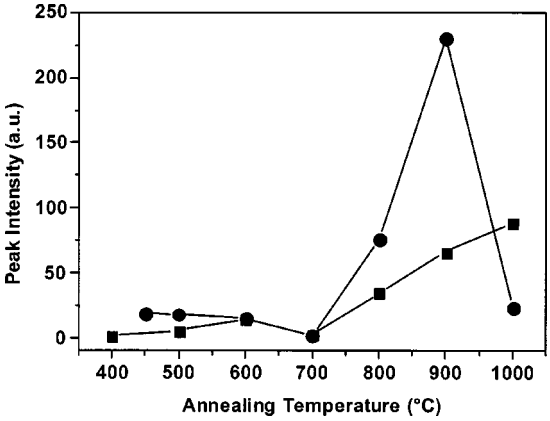

FIG. 1. Peak intensities versus annealing temperatures. Dots show the intensities for the hydrogenated samples (set 1), square symbols represent the reference samples of set 4.

For low annealing temperatures ($<600\,^{\circ}$C), we find a slightly enhanced PL intensity of hydrogenated sample (set 1) in comparison to the reference sample (set 3). The luminescence drops for annealing temperatures between 600 and 700 °C and rises again for higher annealing temperatures. Whereas in the reference samples (set 3 and 4), this rise is monotonic, the yield in the hydrogenated samples shows a sharp increase up to 900 °C and then drops again for 1000 °C (Fig. 1). Figure 1 shows a comparison of peak intensities versus annealing temperature for samples of sets 1 and 4. The reference sample was chosen in spite of its different preparation because it showed the largest PL yield measured so far at our institute. Samples of set 2 show similar behavior but less intense PL. The largest effect of hydrogenation is found in samples previously treated with SPE (set 1). Here, the luminescence yield for an annealing temperature of 900 °C is five times larger than in samples without hydrogen. Another significant difference is found in the number of lines in the spectra. For annealing temperatures above 700 °C, the so-called cubic center, represented by five characteristic lines, appears and becomes more and more dominant. The previously observed lines for samples with similar high Er concentrations due to Er–O complexes are completely absent (see Fig. 2).[11]

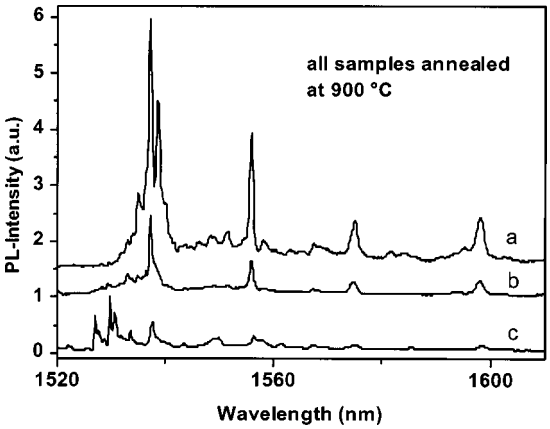

FIG. 2. (a) The cubic lines dominate the PL spectra in the hydrogenated samples. (b) Spectra of a sample with low Er concentration and (c) of a reference sample (set 4) are shown. The lines at 1.53 μ m due to Er–O complexes are absent in the hydrogenated sample. Spectra are shifted for clarity.

Since hydrogen is known to enhance the diffusion constant of several impurity species in silicon, we investigated the local concentration of our dopants in the samples of set 1 by applying secondary ion mass spectrometry (SIMS). Previous SIMS measurements on samples of sets 3 and 4 showed Gaussian profiles with no significant diffusion of the doping species, in accordance with results found in the literature.[12] The results obtained on samples of set 1 showed, however, that the usual Gaussian doping profiles are strongly modified. We find a highly doped surface layer with concentrations of Er and O reaching peak values of more than 10^{20} cm^{-3}. These results match with the drop in luminescence yield for samples annealed at 1000 °C. For the latter, in the absence of hydrogen, we earlier observed luminescence mainly from Er incorporated in oxygen precipitates.[7] Our present result is expected since, due to the enhanced diffusion of oxygen in the presence of hydrogen, most of the oxygen has diffused to the surface. Therefore, the formation of these precipitates is limited to a shallow surface layer with its nonideal concentrations of Er and O.[6] The appearance of the cubic center is unexpected, however. This center is attributed to Er on an interstitial site,[11] and is usually only observed in samples with low Er concentration. In order to gain information on the origin of the PL, we created an "optical depth profile" by removing thin layers from the surface of samples from set 1 using reactive ion etching. Removing 60 nm from the top of the sample corresponds to a removal of 80% of the incorporated erbium according to the measured SIMS profile. Surprisingly, the luminescence yield dropped by only 10%. This result indicates that the luminescence originates from deeper regions with lower Er concentration. Using the implantation dose and the SIMS results, we estimate the remaining concentration of erbium in the sample to be in the area of 3×10^{12} cm^{-2}.

So far, without hydrogenation, maximum PL yield for the cubic center was achieved for Er implantation energies of 300 keV, a dose of 1×10^{13} cm^{-2}, and an annealing temperature of 900 °C.[11] Comparing the intensity of our hydrogenated samples to samples implanted with 1×10^{13}-cm^{-2} Er (set 5), we find again a significantly higher intensity in the hydrogenated samples, pointing to a higher percentage of optically active erbium in the hydrogenated samples. Studies of the dependence on excitation power and lifetime support this interpretation. In the high-power regime, the PL yield I_{Pl} is given by

$$I_{\mathrm{PL}} \propto N_{\mathrm{Er}}^{*}/\tau, \tag{1}$$

with N_{Er}^{*} being the number of optically active erbium centers and τ their radiative lifetime. The hydrogenated samples show a higher saturation intensity compared to both the reference sample and samples optimized for cubic center luminescence. The comparison to the reference sample of set 4 is justified here, in spite of the different emitting centers, since the lifetime is identical for both centers.[13] The higher saturation intensity demonstrates a higher number of optically active erbium ions. The "thermal" quenching of the PL intensity with increasing temperature is not influenced by hydrogen. Thus, additional codoping with hydrogen does not help with RT applications. It may, however, be advantageous

for applications at low temperatures making use of the higher percentage of optically active erbium and the narrow linewidth[11] of the cubic center.

In summary, hydrogen influences the PL of Si:Er,O indirectly by mobilizing the implanted Er and oxygen. SIMS measurements give evidence for an enhanced diffusion of both species at elevated temperatures towards the surface. Subsequently, the local concentration of both dopants is changed. This change in local concentration leads to a dominance of the cubic center usually found only for lower Er concentrations. We find a substantial increase of the luminescence yield for annealing temperatures in the range of 800 to 900 °C. The luminescence yield in the hydrogenated samples is significantly higher even if compared to samples prepared to optimize the cubic center luminescence. Comparing luminescence yield and local concentration, we obtain strong indications for an enhanced solubility of the cubic center in samples codoped with hydrogen.

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